

Electronic Supplementary Information

Exopolyhedral ligand flipping on isomerisation of novel supraicosahedral stannacarboranes

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1. Synthetic Procedures

Synthesis of **1**: Sodium (0.19 g, 8.13 mmol) reduction of 1,12-Me₂-1,12-*closo*-C₂B₁₀H₁₀ (0.20 g, 1.16 mmol) in liquid ammonia (ca. 20 mL) at -78°C for 4 h yielded a dark blue solution. Removal of ammonia upon warming allowed the dry residue to be extracted into degassed THF (20 mL). The grey suspension was filtered into a Schlenk tube under nitrogen affording a clear solution, which was transferred via cannula to a THF (20 mL) solution of SnCl₂ (0.22 g, 1.16 mmol) frozen to -196°C. The mixture was slowly warmed to RT with stirring. Volatiles were removed in vacuo, DCM added, and the product filtered. The filtrate was evaporated to afford a white solid, recrystallised from DCM/petroleum ether to yield colourless crystals.

Yield 71 mg (21%). Mass spectrometry: *m/z* envelope centred on 289 (M⁺). Microanalysis: Theoretical; C 16.51, H 5.54. Found; C 16.30, H 5.64%. IR (DCM): ν_{\max} 2552 cm⁻¹ (B-H). NMR data are given in the manuscript. Although there are fewer resonances in both the ¹¹B{¹H} and {¹H} spectra than might have been anticipated for a molecule with, in solution, effective C_s symmetry, there is no feasible fluxional process that would afford a higher degree of symmetry. Certainly, in the analogous compound 1,10-Me₂-4- η -C₆H₆-4,1,10-RuC₂B₁₀H₁₀ (Compound **10** in Welch, et al, *Chem. Commun.*, 2005, 1348) there are six ¹¹B signals in the ratio 2:2:1:1:2:2 and two CH₃ signals in the ¹H spectrum.

Synthesis of **2**: A stirring degassed toluene solution (5 mL) of Me₂bipy (20 mg, 0.11 mmol) was treated with a toluene solution (10 mL) of **1** (30 mg, 0.10 mmol) at room temperature. A bright yellow precipitate formed instantaneously. Toluene was removed and the resulting solid washed with petroleum ether (2×10 mL) and dried in vacuo. Crystallisation from DCM/petroleum ether.

Yield 20 mg (42%). Microanalysis: Theoretical; C 40.44, H 5.94, N 5.89. Found; C 39.85, H 5.76, N 5.72%. IR (DCM): ν_{\max} 2521 cm⁻¹ (B-H). Again, NMR data are given in the manuscript. It is possible that the Me₂bipy ligand in **2** is flipping between alternative orientations in solution at room temperature (trans to C1 and trans to C10) but we have no evidence for that.

Synthesis of **3**: A degassed toluene solution (20 mL) of **1** was heated to reflux for 3 h. After cooling to RT the solution was filtered and the solvent removed. Following washing with petroleum ether (2×20 mL) and drying in vacuo, the product was afforded as a white solid.

Yield 288 mg (66%). Mass spectrometry: *m/z* envelope centred on 289 (M⁺). IR (DCM): ν_{\max} 2544 cm⁻¹ (B-H).

Synthesis of **4**: A stirring degassed toluene solution (3 mL) of bipy (6 mg, 0.04 mmol) was treated with a toluene solution of **3** (10 mg, 0.03 mmol) at room temperature. A pale yellow precipitate formed instantaneously. Toluene was removed and the resulting solid washed with petroleum ether (2×10 mL) and dried in vacuo. Crystallisation from DCM/petroleum ether.

Yield 4 mg (30%).

2. Additional Crystallographic Information

Intensity data were collected from single crystals on a Bruker X8 APEX2 diffractometer, with crystals mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Empirical absorption corrections were made using the program SADABS¹. The

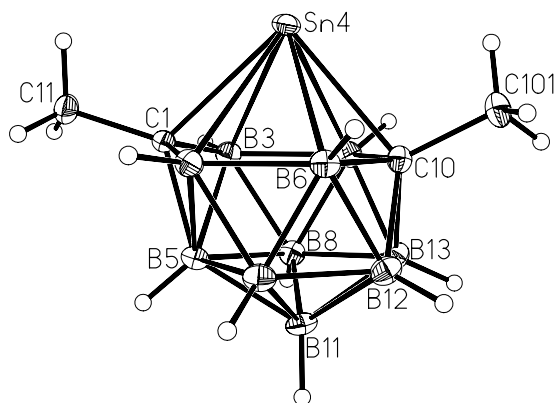
structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL program suite.² All non-hydrogen atoms were refined with anisotropic displacement parameters. In **2** there is rotational disorder of the methyl groups of the Me₂bipy ligand and a partially disordered CH₂Cl₂ of solvation. In **4** there is partial disorder in the cage, with a {CMe} unit being 67:33 in cluster vertices 12 and 13, respectively, complemented by {BH} being 33:67 at positions 12 and 13.

1 SADABS, V2.05; G. M. Sheldrick, University of Göttingen, Germany, 2005.

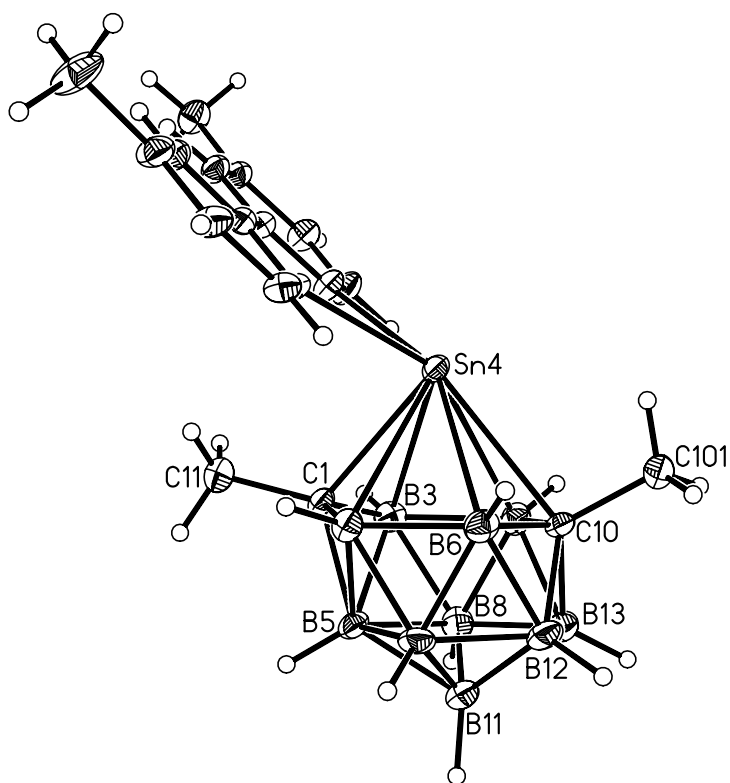
2 SHELXTL, V6.10; Bruker-AXS, Madison, WI, USA, 2000.

In the views below all non-H atoms are shown with 50% probability ellipsoids.

View of 1



View of 2



View of 4

